

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

**NASA TECHNICAL
MEMORANDUM**

NASA TM X-71817

NASA TM X-71817

(NASA-TM-X-71817) SPECTRAL REFLECTANCE
PROPERTIES OF ELECTROPLATED AND CONVERTED
ZINC FOR USE AS A SOLAR SELECTIVE COATING
(NASA) 14 p HC \$3.50

CSCI 10A

N76-13593

Unclassified
G3/44 05370

**SPECTRAL REFLECTANCE PROPERTIES OF ELECTROPLATED AND
CONVERTED ZINC FOR USE AS A SOLAR SELECTIVE COATING**

by Glen E. McDonald and Henry B. Curtis

Lewis Research Center
Cleveland, Ohio 44135

and

Louis Ganelos
Harsaw Chemical Company
Cleveland, Ohio 44106

TECHNICAL PAPER presented at
International Solar Energy Society
Los Angeles, California, July 27 - August 1, 1975



SPECTRAL REFLECTANCE PROPERTIES OF ELECTROPLATED AND
CONVERTED ZINC FOR USE AS A SOLAR SELECTIVE COATING

by Glen E. McDonald and Henry B. Curtis

NASA-Lewis Research Center
Cleveland, Ohio

and

Louis Ganelos
Harshaw Chemical Company
Cleveland, Ohio

ABSTRACT

The spectral reflectance properties of electroplated and chemically converted zinc were measured for both chromate and chloride conversion coatings. The reflectance properties were measured for various times of conversion and for conversion at various chromate concentrations.

The values of absorptance, α , integrated over the solar spectrum, and of infrared emittance, ϵ , integrated over black body radiation at 250° F were then calculated from the measured reflectance values.

The interdependent variations of α and ϵ were plotted. The results indicate that the optimum combination of the highest absorptance in the solar spectrum and the lowest emittance in the infrared of the converted electroplated zinc is produced by chromate conversion at 1/2 concentration of the standard NEOSTARTM chromate black solution for 0.50 minute or by chloride conversion for 0.50 minute.

INTRODUCTION

The NASA-Lewis Research Center is conducting research on solar collectors as part of the national program to develop new energy sources. In order to achieve maximum efficiency at high collector plate temperatures it is important that the collector have a "selective" coating - one that has both the maximum possible absorptance across the solar spectrum and the minimum possible emittance in the infrared (ref. 1).

In addition to the requirement for maximum efficiency, a practical solar selective coating must have comparative ease of application, wide availability and low cost. We have previously determined that a widely available, commercial, decorative electroplated black chrome finish has the desired solar selective properties of high absorptance in the solar spectrum and low emittance in the infrared (ref. 2).

In the present research we have determined that another commercial decorative finish--chemically converted electroplated zinc- also has desirable solar selective properties.

The conditions were investigated for the chemical conversion of the electroplated zinc which would produce the "optimum solar" selective properties; namely, the best combination of a high absorptance and low emittance. The particular electroplating zinc compound used in this study is available as a proprietary material from the Harshaw Chemical Co., but the results obtained should be generally indicative of the properties obtainable from this general class of coatings. Visible and infrared spectral reflectance were measured to determine the performance potential of this kind of solar selective coating.

This paper describes the method of producing the black coating on zinc, the results of the measurements of the spectral reflectance, and the calculated values of absorptance and emittance of interest for the solar coating application.

DESCRIPTION OF SPECTRAL MEASUREMENTS

All measurements reported are hemispherical diffuse reflectance.

The spectral reflectance from 0.35 to 2.1 microns of the black coating was measured with a Cary-14 spectrophotometer with a spherical diffuse reflectance attachment. A calcium carbonate (CaCO_3) surface prepared at the NASA-Lewis Research Center was used as a standard.

The spectral reflectance from 0.3 to 18.0 microns was measured with a Willey 318-A spectrophotometer using a spherical diffuse reflectance attachment. The Willey 318-A is a Michelson interferometer type of spectrophotometer. Evaporated gold film was used as a standard. Evapo-

rated aluminum on glass was used as a secondary standard. The accuracy of measurement is estimated to be ± 0.02 units of emittance.

DESCRIPTION OF BLACK COATING PREPARATION

In this investigation, the black coating was produced on 4×6 inch test panels. These panels were 1020 cold rolled steel polished on one surface to a roughness of less than $1/2$ micro-inch RMS. This type of panel is regularly furnished by Apollo Steel as a standard test coupon for the electroplating industry. However, the only significance for this investigation was that the panels formed a convenient base for the test of electroplating conditions.

The panels were first plated with approximately 0.0002 inch of bright zinc from Harshaw Chemical Co. (NEOSTARTM-AFA, ammonium free acid zinc). Next the zinc was converted to solar selective conditions with an appropriate chemical treatment. This changed the bright, metallic, specular zinc into a black state, which varied in appearance depending on the materials and conditions used in the conversion.

The panels were plated in the following sequence.

(1) Cleaned by electrolytic alkaline chelating cleaner at 190° F and 70 to 80 amps/ft². Two cycles, interspersed with acid, were used.

(2) Zinc was plated from Harshaw Chemical Company NEOSTARTM-AFA at 2.4 volts and 40 amps/ft² for 10 minutes to produce approximately 0.0002 inch of zinc.

(3) Water rinsed.

While still wet the zinc was chemically treated to produce a solar selective state by dipping the panel in a water solution of an appropriate compound and agitating for the time used for conversion.

The conversion followed the following sequence:

- (1) Dip in solution of conversion compound, with agitation, for the appropriate time
- (2) Water rinse.
- (3) Air dry.

The panels as prepared, were wrapped in tissue and stored until spectral measurements were completed.

TEST RESULTS

The electroplated zinc was converted to a black state for study of solar selective properties by treatment with either of two chemicals: Harshaw Chemical Company NEOSTARTM -Chromate Black or NEOSTARTM -Chloride Black.

In the study of both of these conversions, the solar selective properties were measured as a function of time of conversion treatment. In addition, the spectral properties produced by the chromatic conversion were measured for three different concentrations of chromate. The standard chromate conversion was so rapid and time so critical that it was necessary to investigate sub-normal concentrations. The chloride conversion produced a satisfactory range of results at normal concentration.

Chromate Conversion

The chromate conversions were made at 50%, 75%, and 100% and full concentrations of that normally used for NEOSTARTM -Black Chromate. At all of these concentrations, and with normal temperature and agitation, the conversion of the zinc to a black state proceeds very rapidly. At all of these concentrations, conversions were made for immersion times of 0.25, 0.5, 0.75, 1 and 2 minutes. For increasing times the general appearance of the panels varied from red through violet colors to jet black. The colors produced at the shorter conversion times are due to interference effects and on a typical panel the color fringe was up to two inches in width. The spacing of the color fringes indicates a uniformity of conversion treatment.

The appearance of the panels produced by the chromatic conversion is summarized in Table I. The separation between color fringes and production of jet black has been indicated by the heavy line. The location of the line indicates that at the full concentration of chromate conversion chemical, there is an extremely rapid reaction which progresses from the production of color to production of jet black appearance.

The results of the spectral measurements of reflectance of the chromate conversion of electroplated zinc as a function of wave length are

shown in figures 1(a), 2(a), and 3 for chromate concentrations of 50%, 75%, and 100%, respectively. Curves for 1 and 2 minute conversion time overlap the other data and are therefore not shown.

The spectral reflectance curves for the converted zinc may be compared in each figure with the reflectance of plated, unconverted zinc and with the reflectance of an idealized solar selective surface.

In general there is a very rapid decrease in visible reflectance produced by the chromate conversion of plated zinc. This occurs at the lower concentrations and shorter times without an appreciable decrease in infrared reflectance. The lower concentrations and lower times produce distinct interference patterns in the curves of reflectance. These confirm that the colors observed in the visual observation are due to interference effects. At higher concentrations and longer times the interference patterns become progressively weaker. Correspondingly the colors in these panels are weaker.

The infrared region from 2 to 18 microns is characterized by deep absorption bonds at the positions occupied by H_2O . The chromate conversion of the zinc produces a gel structured zinc chromate which contains H_2O in the gel lattice. Although a number of weeks elapsed between coating preparation and reflectance measurement, the H_2O was retained since it was locked into the gel structure.

Subsequent to measurement the coated samples were heated for 24 hours at $120^{\circ}C$ at a pressure of 200 microns and then were remeasured. The results are shown in figures 1(b) and 1(c) for 1/2 concentration conversion. At the lower times and concentrations of conversion and, therefore, the thinner black chromate coatings, this treatment effectively removes the chemisorbed water, as shown by the disappearance of the absorption bands in figure 1(b), and therefore improves the emittance characteristics. With heavier coatings only a partial improvement in emittance is obtained as shown in figures 1(c) and 2(b).

Several months subsequent exposure of the baked coatings to normal but frequent highly humid atmosphere did not result in an increase in emittance for the vacuum baked samples.

The values for the absorptance integrated over the solar spectrum and the values of the integrated infrared emittance are shown in Table II. The emittance measured after vacuum bake-out are shown in parentheses. The values of absorptance and emittance for the black chromate produced by the chromate conversion are plotted in figure 4. From this plot it is seen that:

- (1) All concentrations of chromate used for conversion produce values of α and ϵ which fall along a smooth line.
- (2) Maximum absorptance, without accompanying serious increase in emittance, is reached in times as short as 1/2 minute, even at the dilute 50% concentration. 75% and 100% concentration conversions produce excessive emittance at times over 1/4 minutes.

Therefore, since there is no change in mechanism of production of solar selective coatings at different concentrations of chromate, and since optimum values of emittance are rapidly exceeded, only 50% concentration should be used.

Chloride Conversion

All chloride conversion was made at full concentration normally used for NEOSTARTM-Black Chloride. At this concentration and with normal temperature and agitation the conversion of the zinc proceeds very rapidly, but at a rate such that the results can be controlled by varying time. The general appearance of the chloride converted zinc is different from the chromate converted zinc. Whereas the chromate conversion, at all concentrations and at all conversion times, produces a specular surface--in either the color-fringe version or the jet black phase--the chloride conversion produces a dull surface consisting of smutty particles which can be rubbed off. The reflectance of the chloride-converted zinc is shown as a function of wavelength in figure 4. The reflectance curve of the chloride-converted zinc shows no pronounced interference effects.

The values for the integrated absorptance and emittance for the chloride conversion are given in Table II and are plotted in figure 6. The same interdependence of emittance and absorptance exists as was previously shown for the chromate conversion (fig. 5) and for black chrome (ref. 2).

Comparison of the chloride conversion to the chromate conversion shows that while the chloride conversion produces a loosely adherent reaction product that is more easily mechanically disturbed than the hard, specular reaction product produced by the chromate conversion, the chloride conversion produces higher values of absorptance at lower values of emittance.

The chloride conversion of the zinc is a replacement reaction and produces a copper compound which acts as the absorbing medium in the visible spectrum. This material does not have the gel structure of the zinc chromate and therefore does not have the infrared absorption bands characteristic of the chemisorbed water.

Reflectance versus wave length for black coatings, with both chloride and chromate conversion are shown in figure 7. For comparison, previously measured values for black chrome (ref. 2) are also shown.

Discussion

Both the chromate and the chloride conversion of electroplated zinc produce solar selective surfaces of high absorptance and low emittance. For a range of times and concentrations of conversion the optimum values produced by chromate conversion were $\alpha = 0.79$ and $\epsilon = 0.07$ and the optimum values produced by chloride conversion were $\alpha = 0.93$ and $\epsilon = 0.08$. The chromate conversion produces a hard, adherent coating characterized by variations in color produced by interference effects and also by infrared absorption bonds due to chemisorbed water in the zinc chromate gel structure; the chloride conversion produces a soft, black deposit. There is no information available on the stability of these zinc conversion coatings at the conditions of solar collector use.

SUMMARY OF RESULTS

Measurements of the spectral reflectance over a range from 0.35 to 18 microns of black coatings prepared by both chromate and chloride conversion at times ranging from 0.25 to 2 minutes, and calculation of the integrated absorptance over the solar spectrum and of infrared emittance

indicates that black coatings can be produced in a form which has desirable solar selective properties. The optimum chromate conversion had values of $\alpha = 0.79$ and $\epsilon = 0.07$, and the optimum chloride conversion had values of $\alpha = 0.93$ and $\epsilon = 0.08$. These values are in the range of those of other solar selective coatings such as black chrome (ref. 2) and indicate that converted zinc might be added to the list of available solar selective coatings.

REFERENCES

1. Tabor, H.: Selective Radiation. I - Wavelength Descriimination. Transactions of the Conference on the Use of Solar Energy. Vol. 2, Pt. 1, Sec. A, F. Carpenter, ed., University of Arizona Press, 1958, pp. 24-33.
2. McDonald, Glen: Variation of Solar-Selective Properties of Black Chrome with Plating Time. NASA TM X-71731, 1975.

TABLE I. - APPEARANCE OF CHROMATE CONVERSION PANELS

		Conversion time, minutes				
		0.25	0.50	0.75	1	2
50% Concentration	Colored	Colored	Black	Black	Black	Black
75% Concentration	Colored	Colored	Black	Black	Black	Black
100% Concentration	Colored	Black	Black	Black	Black	Black

TABLE II. - SOLAR SPECTRUM ABSORPTANCE AND INFRARED
EMITTANCE OF BLACK ZINC AT VARIOUS CONVERSION TIMES

Conversion	Conversion time, minutes					
	Absorptance emittance	0.25	0.50	0.75	1.0	2.0
Chromate	α	0.79	0.87	0.92	0.93	0.92
	ϵ	0.07 (0.05)	0.21 (0.10)	0.59 (0.37)	0.80 (0.73)	0.69 (0.53)
Chromate	α	0.89	0.94	0.93	0.93	0.93
	ϵ	0.18 (0.09)	0.61 (0.35)	0.70 (0.46)	0.74 (0.61)	0.81 (0.77)
Chromate	α	0.91	0.93	0.92	0.93	0.93
	ϵ	0.29 (0.20)	0.71 (0.70)	0.68 (0.60)	0.82 (0.82)	0.85 (0.84)
Chloride	α	0.93	0.95	-----	0.96	0.97
	ϵ	0.08	0.12	-----	0.21	0.73

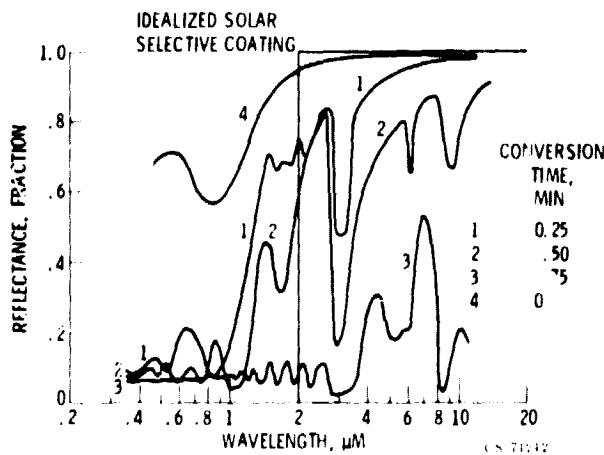


Figure 1(a). - Reflectance of black zinc produced by 50% concentration chromate conversion.

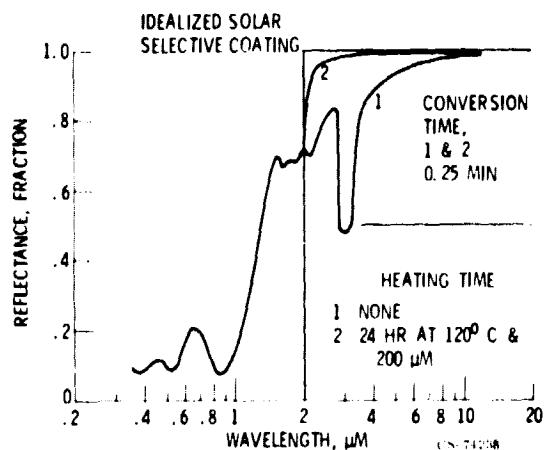


Figure 1(b). - Continued. Reflectance of black zinc produced by 50% concentration chromate conversion.

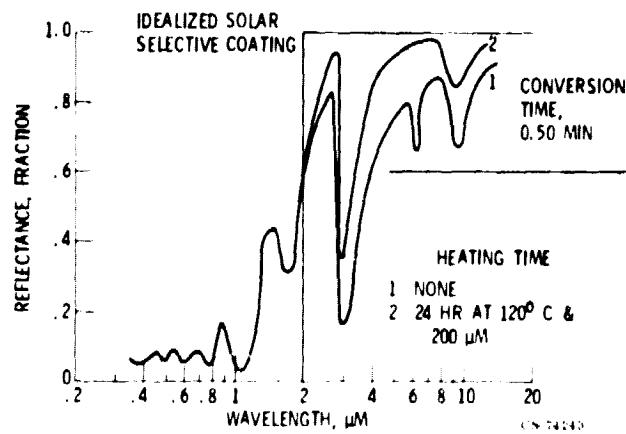


Figure 1(c). - Concluded. Reflectance of black zinc produced by 50% concentration chromate conversion.

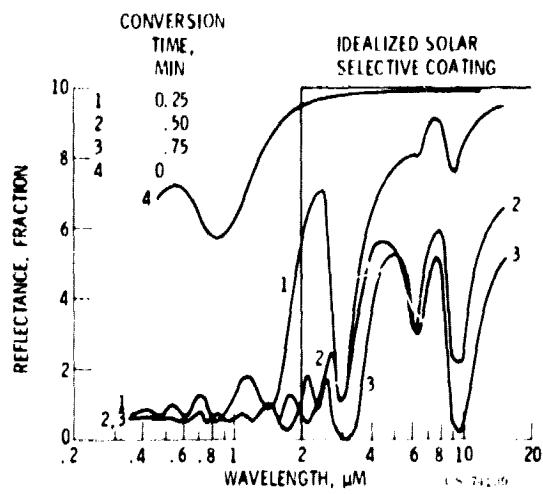


Figure 2(a). - Reflectance of black zinc produced by 75% concentration chromate conversion.

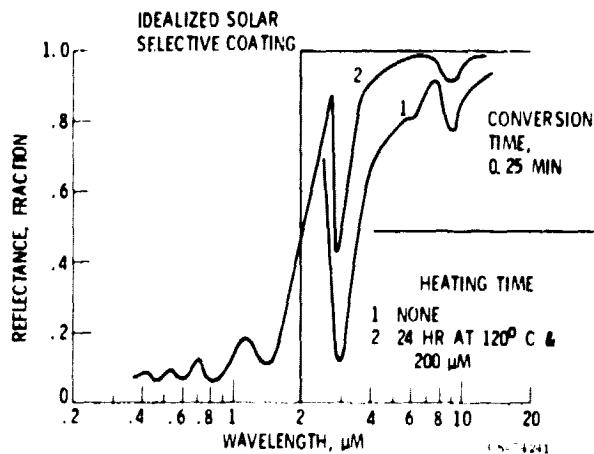


Figure 2(b). - Concluded. Reflectance of black zinc produced by 75% concentration chromate conversion.

ORIGINAL PAGE IS
OF POOR QUALITY

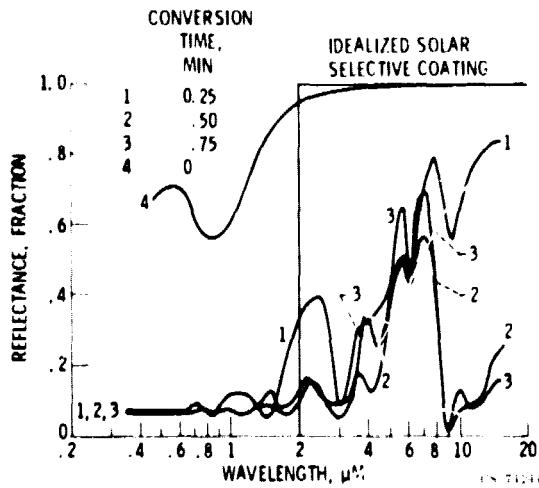


Figure 3. - Reflectance of black zinc produced by 100% concentration chromate conversion.

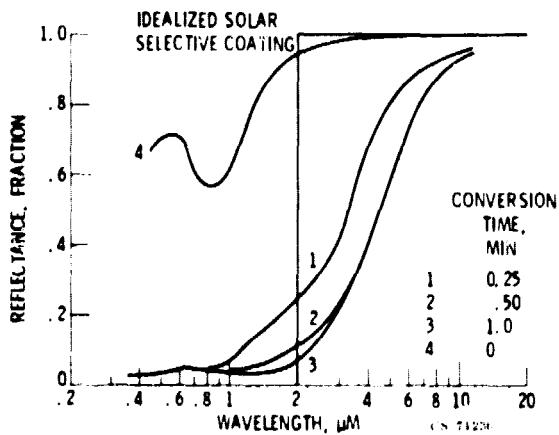


Figure 4. - Reflectance of black zinc produced by chloride conversion.

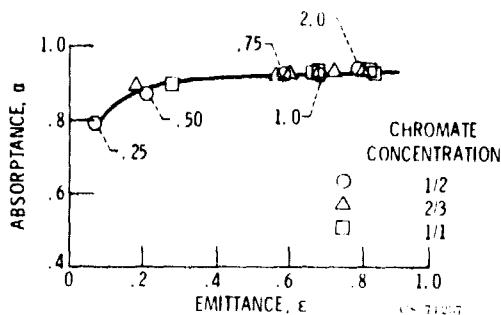


Figure 5. - Solar spectrum absorptions vs. infrared emittance for black zinc produced by chromate conversion. Conversion time indicated in minutes for chromate conversion at 50% concentration only.

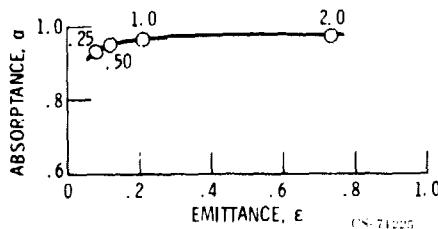


Figure 6. - Solar spectrum absorptance vs. infrared emittance for black zinc produced by chloride conversion. Conversion time indicated in minutes.

- 1 BLACK ZINC
CHROMATE CONVERSION
- 2 BLACK ZINC
CHLORIDE CONVERSION
- 3 BLACK CHROME

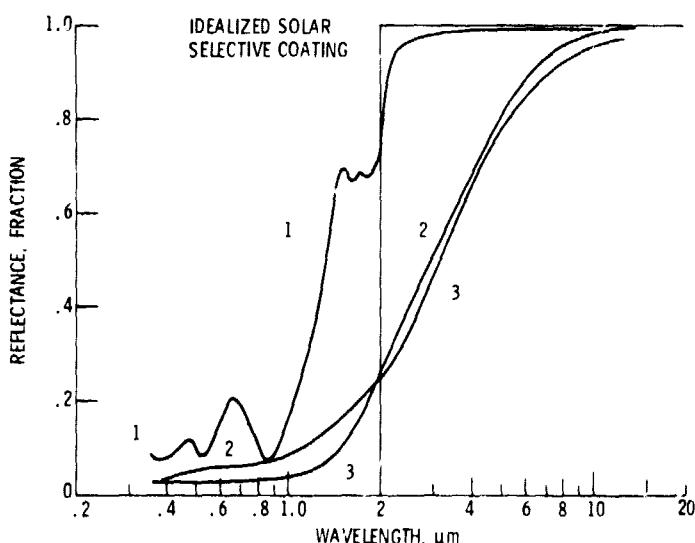


Figure 7. - Reflectance of black zinc and of black chrome solar selective coatings.